

# Ion Exchanger Catalysts

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This short review discusses specific properties of ion exchanger catalysts in which these polymer-based materials differ from conventional heterogeneous catalysts based mostly on inorganic supports. A good understanding of these effects may help to optimize catalysts for specific process conditions.

Key words: *Ion exchanger, catalyst, heterogenization, acid, properties*

Strongly acidic ion exchangers can replace soluble acids as catalysts in many industrially important reactions. Heterogenization of the homogeneous catalysts makes it possible to minimize wastes and replace batch reactors with continuously operated flow-through reactors. Ion exchangers have been used in a number of industrial processes. Examples of industrially important processes include synthesis of methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME), esterification of acrylic acid, alkylation of phenol, hydration of olefins, dehydration of alcohols, etc. In some processes the acid groups are supplemented with some other functionality acting as a promoter, e.g. mercapto groups in the catalysts for synthesis of bisphenol A or as catalysts of different type reactions, for example bifunctional palladium-containing ion exchanger catalysts for synthesis of methyl *iso*-butyl ketone (MIBK) or TAME. A few reviews on the catalytic applications of ion-exchanger resins exist in the literature (see for example)<sup>1,2</sup> however, none of them treats the subject from the viewpoint of relations between the resin morphology and catalytic properties.

All industrially important ion exchanger catalysts are sulphonated styrenic polymers. From the chemical point of view, they have a well-defined nature – their building block is  $-\text{SO}_3\text{H}$  group bonded to aromatic ring. However, the uniformity of chemical composition does not mean uniformity of their application properties. Catalytic activity of various types of the strongly acidic ion exchange resins can be very different. Responsible for these variations are differences in the morphology of their polymer skeletons. With regard to the relations between morphology and application properties of polymer catalysts, we must view parameters like surface area or porosity from a different perspective than in the case of catalysts based on inorganic carriers.

While classical inorganic catalyst reactions proceed on the well-defined interface between solid and fluid phase, with ion exchanger catalysts the reactions proceed inside the swollen polymer gel. The swelling of ion exchangers in contact with reaction environment is a key factor for the

accessibility of the catalytic active centres. This is true not only for the so-called “gel-type” ion exchangers but also for the “macroreticular” (or “macroporous”) types. In macroreticular ion exchangers exists a porosity independent of the swelling of the polymer mass, but only an insignificant portion of active groups is located on the walls of the “true” pores – in typical industrially important ion exchanger catalysts like Amberlyst 15 or Lewatit SPC118 it is less than 5 %. Morphology changes due to swelling of ion exchangers are schematically shown in Fig. 1.

The network of the “true” pores in macroreticular ion exchanger catalysts has probably greater importance as a means of facilitating swelling in poor solvents than a key factor in transport of reactants.

In the majority of cases, ion exchanger catalysts have lower activity than an equimolar amount of soluble strong acid and diffusional hindrances are mostly blamed for this. However, frequently this is not the true reason. Experiments in which the catalyst particle size was varied only rarely showed significant influence of this parameter on the catalytic activity. For illustration of the properties and problems of practical application of ion exchanger catalysts, a case study of synthesis of bisphenol A will be used in this

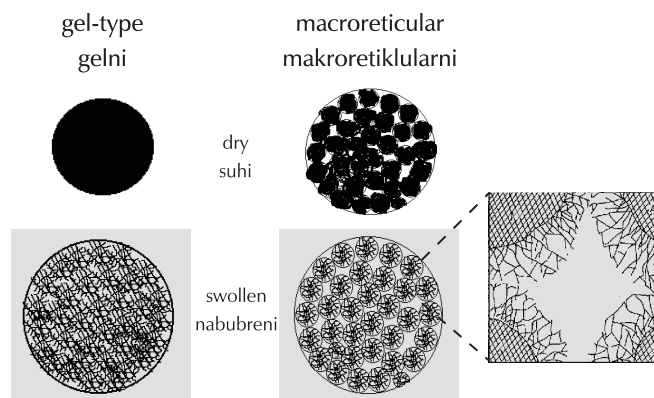


Fig. 1 – Dry and swollen-state morphology of gel and macroreticular ion exchangers

Slika 1 – Morfologija suhih i nabubrenih gelnih i makroretikulárních ionských izmjenjivača

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text. For this reaction, our own experiments indicated that some diminishing of reaction rate was observed only when catalyst particle size was greater than about 0.8 mm<sup>3</sup> (Table 1).

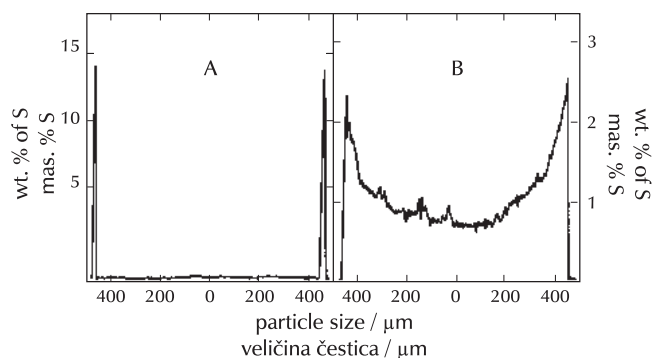
**Table 1** – Dependence of the reaction rate of bisphenol A synthesis on the particle size of the catalyst. Catalyst: gel-type resin cont. 4 % divinylbenzene, 15 % of acidic groups neutralized by cysteamine. Molar ratio of acetone : phenol = 1 : 8; temperature 70 °C.

**Tablica 1** – Ovisnost brzine sinteze bisfenola A o veličini čestica katalizatora. Katalizator: gelna smola s 4 % divinilbenzena; 15 % kiselih skupina neutralizirano cisteaminom. Molarni omjer acetona : fenol = 1 : 8; temperatura 70 °C.

Particle size / mm Veličina čestica / mm	<i>r</i> / mmol g <sup>-1</sup> h <sup>-1</sup>
0.8	19.2
0.63 – 0.80	30.3
0.35 – 0.63	28.2
0.22 – 0.35	31.8

Majority of particles in commercial ion exchangers is smaller than 0.8 mm and hence, on the path between surface and the interior of the particle, the influence of internal diffusion in the classical sense, is not an important factor. Nevertheless, it is unquestionable whether morphology of the polymer backbone has great importance for application properties of ion exchanger catalysts. However, predominantly it is the local density and configuration of the swollen polymer matrix controlling microreactor environment in which the catalytic centres operate. It could be illustrated on the examples of two differently sulphonated ion exchanger catalysts.<sup>4</sup> The first sample (A) was sulphonated a short time at high temperature. Sulphonation of the polymer beads was only limited to surface layers at these conditions. Concentration of sulphur in these layers measured by electron microprobe (Fig. 2) corresponded to the full sulphonation of the polymer mass in this region. The second sample (B) was sulphonated at laboratory temperature after pre-swelling of the polymer in dichloroethane. At these conditions, the interior of the polymer beads was also sulphonated. However, as seen by the electron microprobe, the resulting sulphur concentration was much lower (Fig. 2). It does not explicitly mean that the local degree of sulphonation was actually so low. More probably, fully sulphonated domains were intermixed with the unsulphonated polymer so intimately that the microprobe with the resolution of about 1 μm was not able to see them separately.

Catalytic activity of both resins was tested by measurements of initial reaction rates of bisphenol A synthesis. Results of the activity tests are shown in Table 2. Remarkable differences in the specific activity of sulphonic groups of catalyst A and B can be explained by the strong influence of the polymer microstructure on the kinetics. In catalyst B, sulphonic groups were introduced selectively in the most accessible parts of the polymer mass with low local degree of crosslinking where the catalytic reaction can proceed at a high rate. Unsulphonated remained the surrounding poorly accessible domains. In catalyst A, a high



**Fig. 2** – Distribution of sulphur in the particles of A and B ion exchangers evaluated by electron microprobe

**Slika 2** – Raspodjela sumpora u ionskim izmjenjivačima A i B određena elektronskom mikrosondom

number of sulphonic groups were introduced into the skin layer of polymer particles and sulphonated were the low-crosslinked, well accessible parts, and the poorly accessible domains. Sulphonic groups in these dense domains are virtually inactive. The well accessible parts in which the bisphenol A synthesis can proceed, represent only a small fraction of the mass of this polymer. Hence, the activity related to the total amount of the acidic centres is in polymer A much smaller than in polymer B. High specific activity of catalyst B in which most of the active centres are located at a much greater distance from the particle surface than in catalyst A, also demonstrates the negligible influence of intraparticle diffusion. This example illustrates the importance of the local morphology of the polymer carrier for the good functioning of the catalytic activity of the ion exchange resins.

**Table 2** – Catalytic activity of the partially sulphonated gel-type polymer catalysts (8 % DVB) in bisphenol A synthesis

**Tablica 2** – Katalitička aktivnost djelomično sulfoniranih gel-nih polimernih katalizatora (8 % DVB) u sintezi bisfenola A

Catalyst Katalizator	Exchange capacity / meq g <sup>-1</sup> Kapacitet izmjene / meq g <sup>-1</sup>	Initial reaction rate / mmol h <sup>-1</sup> meq <sup>-1</sup> Početna brzina reakcije / mmol h <sup>-1</sup> meq <sup>-1</sup>
A	0.38	0.18
B	0.19	20.90

The key to understanding the relations between morphology and catalytic properties of ion exchange resins is the perception of the fact that in the swollen gel environment, the polymer catalyst and reactants are intermixed really on the molecular level.

The assessment of mutual relations must take into account the mechanism of catalytic reaction, which is different in aqueous and non-aqueous media. In water solutions, the reaction proceeds via mechanism of specific acid catalysis, where the protonating agent is a hydrated proton existing in the gel space as a mobile counterion to the anion –SO<sub>3</sub><sup>-</sup>.<sup>5,6</sup> This situation is schematically depicted in Fig. 3.

The way in which the reacting compounds interact with protonating agent is basically identical with the course of

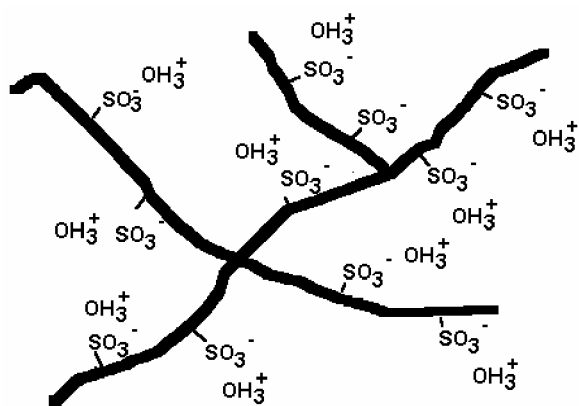


Fig. 3 – Hydrated protons as acidic centres in water-swollen ion exchanger catalysts

Slika 3 – Hidratizirani protoni kao kiselinski centri u ionsko-izmjenjivačkom katalizatoru nabubrenom u vodi

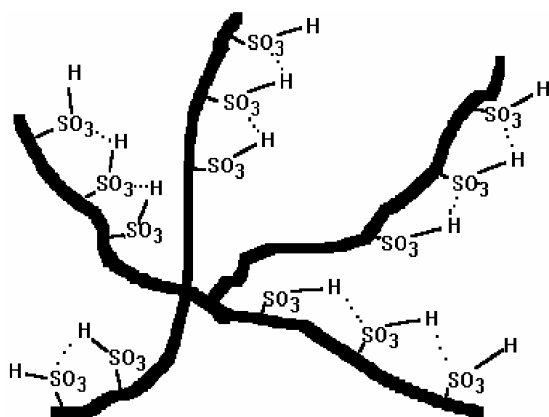


Fig. 4 – Ion exchanger catalyst in a non-aqueous environment

Slika 4 – Ionsko-izmjenjivački katalizator u nevodenom mediju

reaction catalysed by soluble acid. In the aqueous environment, the reaction proceeds by mechanism of homogeneously catalysed reaction in solution, but inside of the swollen polymer gel. The reaction is governed by the concentration of reactants in solution between the polymer chains. The anions bound to the polymer chains do not participate in the reaction and the polymer chains influence the process as inert bodies exercising entropic, steric exclusion effects. This effect begins to diminish the reactant concentration significantly already when the pore is 10-times greater than the reactant molecule. That is why inside the gel of even a highly swollen ion exchanger, the concentration of solutes is substantially lower than in the surrounding liquid. This diminishing of reactant concentration is the basic factor determining the differences between the rate of reaction catalysed with an ion exchanger and that catalysed with a soluble acid.<sup>7</sup>

In a non-aqueous medium, the mechanism of general acid catalysis becomes operative. The reacting molecules are protonated directly by undissociated  $-\text{SO}_3\text{H}$  groups bound to the polymeric chain. Spectroscopic data and measurements of the dependence of catalyst activity on the degree

of neutralization of the ion exchanger by metal cations show that under such conditions the catalytic activity is exercised by ensembles of several  $-\text{SO}_3\text{H}$  groups connected by hydrogen bonds (see Fig. 4).<sup>8</sup>

Catalytic centre is here a part of the polymer chain. In the interactions of reactants with polymer chains within the swollen gel, the enthalpic interactions due to chemisorption on active centres also become important. This attractive force can compensate the steric exclusion (so important in the aqueous environment) and then, the concentration of adsorbed reactants in a narrow pore can be as high as in a wide pore. Of course, this compensation cannot help if a pore is smaller than the approaching molecule; acidic centres located in places too small to accommodate the molecule of reactant or the activated complex are lost for catalytic reaction in such a case.

In Table 3, the activities of various ion exchanger catalysts in three different reactions (and different reaction environments) are compared.<sup>6,9,10</sup>

Table 3 – Relative activities of different ion catalysts in various reactions: A – synthesis of MTBE,  $\text{MeOH} : \text{isobutylene} = 1 : 1$ , B – synthesis of bisphenol A,  $\text{PhOH} : \text{acetone} = 8 : 1$ , C – hydrolysis of saccharose, 20 % of saccharose in water

Tablica 3 – Relativne aktivnosti različitih ionsko-izmjenjivačkih katalizatora u raznim reakcijama: A – sinteza MTBE,  $\text{MeOH} : \text{izobutilen} = 1 : 1$ , B – sinteza bisfenola A,  $\text{PhOH} : \text{acetone} = 8 : 1$ , C – hidroliza saharoze, 20 % saharoze u vodi

Catalyst* Katalizator	DVB content %	$\frac{S_{\text{BET}}}{\text{m}^2 \text{ g}^{-1}}$	Relative activities in reactions: Relativne aktivnosti u reakcijama:		
	Sadržaj DVB-a %				
			A	B	C
SC-102	2	0	0.7	3.0	7.0
SC-108	8	0	0.5	–	–
SPC-108	8	15	1.0	2.0	1.5
SPC-118	18	45	1.0	1.0	1.0
XN-1010	very high / vrlo velik	580	0.3	–	–

\* Catalysts SC... and SPC... are the Lewatit-series products of Bayer, Leverkusen; XN-1010 is the Amberlyst ion exchanger made by Rohm and Haas, USA

\* Katalizatori SC... i SPC... proizvodi su Bayera, Leverkusen, iz serije Lewatit; XN-1010 je ionski izmjenjivač Amberlyst Rohm and Haasa, SAD

From the compared reactions, the strongest influence of the polymer morphology on the catalytic activity was observed for the reaction C – hydrolysis of saccharose, performed in water. Steric exclusion effect, uncompensated by an attractive adsorption interaction with the polymer skeleton was the strongest here, in spite of high swelling of the resins in this environment.

Surprisingly, in the MTBE synthesis, the polymer skeleton morphology has very low influence on the catalyst activity. According to the popular point of view, due to low swelling of ion exchangers in the methanol – isobutylene mixture, the macroreticular resins with extensive swelling-independent porosity should be much better catalysts than the gel-type resins. However, experimental results show small dif-



ferences in the activities of various resins. That is because the attractive forces resulting from enthalpic interactions of reactants with active centres attached to the polymer chains eliminate the steric exclusion effects. For relatively small molecules like methanol, isobutylene or MTBE, only a minimum of active centres is completely inaccessible even in the more crosslinked and less swollen resins. For this reaction, the result is virtual independence of the intrinsic activity of acidic centres on local morphology of the polymer carrier.

Sensitivity of the synthesis of bisphenol A toward the polymer skeleton morphology lays somewhere in-between the above shown examples. Like the MTBE synthesis, this reaction proceeds after adsorption of the reactants on the undissociated sulphonic groups. Also, here is the adverse influence of entropic effect of steric exclusion compensated by enthalpic forces between the reactants and active centres. However, molecules of both starting compounds and the products are rather big, and hence, the higher the local density of the polymer carrier network is, the greater is the probability that some of the acidic centres will be inaccessible for the catalytic reaction. Hence, in the polymers there exist some domains where the bisphenol A synthesis proceeds at much higher reaction rate than in others.

A specific property of ion exchange catalysts is their ability to swell when in contact with the reaction environment. For the gel-type materials, the accessibility of all the usable active centres strongly depends on the swelling of their polymer skeletons. Macroreticular ion exchangers, on the other hand, exhibit a certain amount of porosity that is independent of swelling, and these materials thus remain open even in the dry state. However, with such pores, only a fraction of the supported active groups is directly accessible. Macroreticular ion exchangers also swell in contact with the reaction environment and, in this case, the swelling causes the opening of both additional "true" pores and pores within the swollen polymer gel. The selection of a proper ion exchange catalyst for a particular reaction therefore strongly depends on the ability of the reaction mixture to induce swelling of the catalyst.

Gel-type polymers offer potentially much higher supporting capacities than their macroreticular counterparts. The surface area of polymer chains in styrenic polymers can be as high as  $2000 \text{ m}^2 \text{ g}^{-1}$ .<sup>11</sup> However, a full exploitation of this enormous potential support capacity would require an extremely high expansion (swelling) of the polymer network, which, in turn, would result in unacceptable mechanical properties. Hence, in practical applications, the accessibility of the supported centres is always somewhat limited, depending on the expansion (swelling) of the polymer matrix and the steric demands of a particular reaction (i.e., the molecular size of the reactants and/or the activated complex).

Macroreticular supports contain pores that remain open even in the absence of swelling. In the dry state, commercial ion exchange catalysts exhibit a BET surface area that is usually lower than about  $50 \text{ m}^2 \text{ g}^{-1}$ . Such small surface areas can accommodate only very limited fractions of the supported active centres. In spite of this, this type of catalyst has been used successfully in a number of industrial processes involving reagents in poorly swelling polymer

matrixes. Apparently, in macroreticular catalysts, even poorly swelling solvents are able to cause additional porosity and improve access to more active centres than the size of the dry surface area would suggest. However, the polymer matrix of macroreticular materials is generally much more crosslinked than the polymer mass of the gel types, signifying that in macroreticular materials, even the best swelling solvent can render accessible only a fraction of the amount of active centres that, under similar conditions, are accessible in low-crosslinked polymer gel-type supports. For polar reaction environments, the reasonably swelling polymer matrix of gel-type ion exchange catalysts is definitely the preferred choice. Macroreticular ion exchangers become a viable option when all the reaction components swell the ion exchange catalyst only poorly, e.g., phenol alkylation with olefins, or when the swelling component of the reaction mixture is consumed almost completely during the course of the process, e.g., synthesis of MTBE or ETBE.

Differences between gel and macroreticular morphologies have more influence than the accessibility of the active centres. Changes in the morphology of ion exchange catalysts in response to compositional variations of the reaction environment may influence both the accessibility of the catalytically active centres and the mechanism of their action. A good understanding of these effects may help optimize catalysts for specific process conditions. A reaction system within which a relevant range of reaction conditions is achievable in order to control the swelling of the catalyst polymer matrix is esterification of fatty acids with methanol; the important preliminary step in the production of biodiesel from non-edible, low-cost raw materials.<sup>12</sup> The reaction mixture for the esterification contains basically two types of components: methanol, which is able to swell the ion exchange catalyst, and triglycerides with fatty acids, which have practically no swelling effect whatsoever on the strongly acidic ion exchange catalyst. Changes in the proportions of the swelling and non-swelling components (alcohol/oil ratio) can, in addition to influencing the intrinsic kinetics of the esterification reaction, also affect the working-state morphology of the ion exchange catalyst.<sup>13</sup> The oil and methanol components of the reaction mixture had only limited miscibility. It was possible to achieve a homogeneous solution when the methanol content in the mixture was lower than about 20 %. Above this limit, two separate phases existed in the reaction mixture: a predominant methanol-saturated oil phase, and a small volume of an alcohol-rich phase. This solubility behaviour was the key factor determining the dependence of the catalyst performance on the methanol concentration. Fig. 5 displays the dependence of the stearic acid conversion at a constant reciprocal weight hour space velocity ( $W/F$ , dry catalyst mass/stearic acid moles per volume) for the gel-type ion exchanger Amberlyst BD20.

The methanol concentration influenced not only the intrinsic reaction kinetics, but also the morphology (swelling degree) of the ion exchange catalysts. Catalytic activity of the gel-type ion exchanger catalyst is directly dependent on the extent of the swelling of its polymer matrix. At a concentration of MeOH above 20 wt. %, the reaction conversion was independent of the methanol concentration due to saturation of the catalyst with alcohol. However,

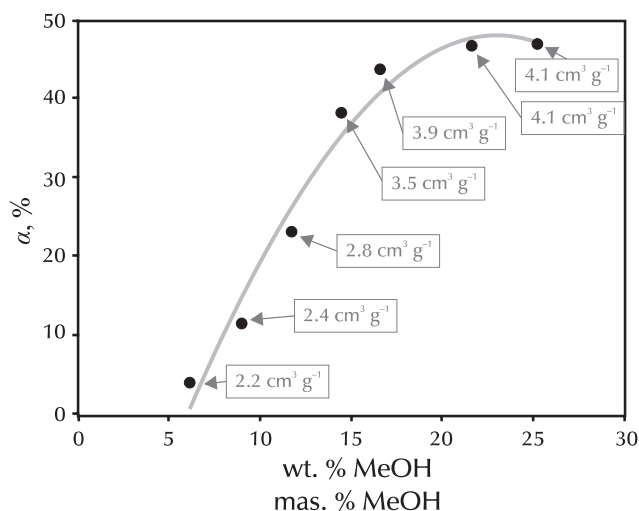


Fig. 5 – Dependence of the stearic acid conversion on the methanol concentration in the reaction mixture comprising the gel-type ion exchange catalyst Amberlyst BD20, together with the specific volume of the catalyst bed in the working state. Temperature 75 °C, 5 wt. % of stearic acid in edible oil,  $W/F = 55 \text{ g h mol}^{-1}$ .

Slika 5 – Ovisnost konverzije stearinske kiseline o količini metanola u reakcijskoj smjesi te specifični volumen zrna gelnog ionsko-izmjenjivačkog katalizatora Amberlyst BD20 u radnom stanju. Temperatura 75 °C, 5 mas. % stearinske kiseline u jestivu ulju,  $W/F = 55 \text{ g h mol}^{-1}$ .

when its concentration was below this limit, the reaction mixture became unsaturated with methanol and the conversion started to fall.

For macroreticular ion exchanger catalysts there was found a different form of dependence of the conversion on the methanol concentration (see Fig. 6). The lowest activity was observed at high methanol concentrations. However, the macroreticular ion exchange catalyst was substantially less active than the gel-type Amberlyst BD20. In order to obtain comparable conversions and therefore carry out all the catalytic tests at similar concentrations of the reaction products, the tests on the macroreticular catalysts were performed at a temperature that was 10 °C higher than that used in the experiments with Amberlyst BD20. In the highly crosslinked macroreticular catalyst, the swellable and hence catalytically active domains form only minor parts of its polymer matrix. Under methanol-saturated conditions, only sulphonic groups occupied with methanol were available for the interaction of the fatty acid molecules with the catalyst. These were located mostly inside the methanol-swollen layer of the polymer matrix, on the walls of the “true” pores (see scheme in Fig. 7). Analogously to general and specific acid catalysis on hydrated and anhydrous sulphonic groups<sup>5,6</sup> (Figs. 3, 4), methanol-occupied sulphonic groups were much less efficient acid catalysts than their “naked” counterparts. As the methanol concentration in the reaction mixture decreased, this layer collapsed. For stearic acid, on the other hand, there was an increased opportunity to compete with methanol for the sulphonic acid groups, which meant a shift from a slower mechanism of specific acid catalysis to a more efficient mechanism of general acid catalysis. With further decrease in methanol concentration the simple effect of lowering of the concentration of one of the key reactants prevails and

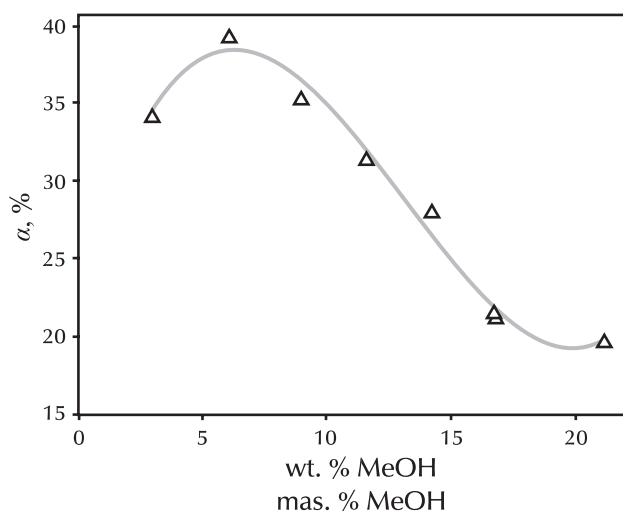


Fig. 6 – Dependence of the stearic acid conversion on the methanol content in the reaction mixtures of the macroreticular ion exchange catalysts crosslinked with 40 % DVB. Temperature 85 °C, 5 wt. % of stearic acid in edible oil,  $W/F = 83 \text{ g h mol}^{-1}$ .

Slika 6 – Ovisnost konverzije stearinske kiseline o količini metanola u reakcijskoj smjesi na makroretikularnom ionsko-izmjenjivačkom katalizatoru umreženom s 40 % DVB. Temperatura 85 °C, 5 mas. % stearinske kiseline u jestivu ulju,  $W/F = 83 \text{ g h mol}^{-1}$ .

that is why the conversion goes through a maximum between 5 – 10 wt. % of methanol in the reaction mixture.

This review attempted to point out some specific properties of ion exchanger catalysts in which these polymer-based materials differ from conventional heterogeneous catalysts based mostly on inorganic supports. A good understanding of these effects may help to optimize catalysts for specific process conditions.

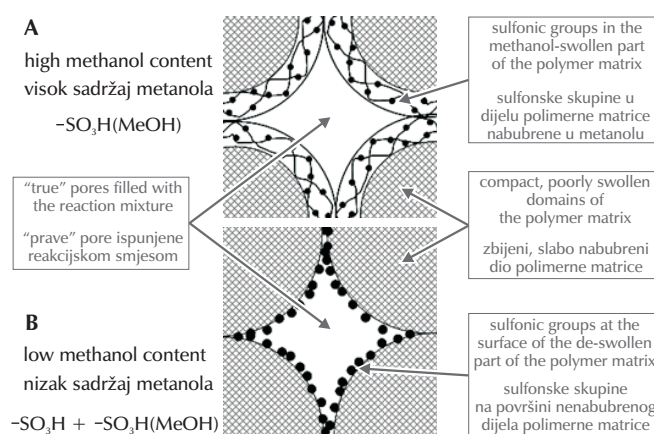


Fig. 7 – A schematic offering a simplified description of the situation for macroreticular ion exchange catalysts in contact with (A) the reaction mixture saturated with methanol and (B) the mixture with a low methanol concentration

Slika 7 – Pojednostavljen shematski prikaz makroretikularnog ionsko-izmjenjivačkog katalizatora u kontaktu s (A) reakcijskoj smjesi zasićenoj metanolom i (B) reakcijskoj smjesi siromašnoj metanolom

## List of symbols and abbreviations

## Popis simbola i kratica

$r$	– reaction rate per catalyst mass, mol g <sup>-1</sup> h <sup>-1</sup> – brzina reakcije po masi katalizatora, mol g <sup>-1</sup> h <sup>-1</sup>
$S_{\text{BET}}$	– specific surface area, m <sup>2</sup> g <sup>-1</sup> – specifična površina, m <sup>2</sup> g <sup>-1</sup>
$\alpha$	– degree of conversion, % – stupanj konverzije, %
BET	– Brunauer–Emmett–Teller
DVB	– divinylbenzene – divinilbenzen
MIBK	– methyl <i>iso</i> -butyl ketone – metil- <i>iso</i> -butil-eton
MTBE	– methyl <i>tert</i> -butyl ether – metil- <i>tert</i> -butil-eter
TAME	– <i>tert</i> -amyl methyl ether – <i>tert</i> -amil-metil eter
W/F	– reciprocal weight hour space velocity, g h mol <sup>-1</sup> – recipročna prostorna brzina, g h mol <sup>-1</sup>

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## SAŽETAK

## Ionsko-izmjenjivački katalizatori

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U ovome su kratkome pregledu razmotrena jedinstvena svojstva ionsko-izmjenjivačkih katalizatora po kojima se ovi polimerni materijali razlikuju od konvencionalnih heterogenih katalizatora uglavnom anorganske osnove. Temeljito razumijevanje utjecaja tih posebnosti može pomoći optimizaciji katalizatora za primjenu u specifičnim procesnim uvjetima.

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